microbalance alternately in an admixed GOD/PEI solution ([GOD]):[PEI]=0.5 mg/ml: 1 mg/ml] and a Mont solution (0.3 mg/ml) for Example 35, and alternately in a GOD solution (0.5 mg/ml) and a Mont solutions (0.3 mg/ml) for Example 36. The resultant frequency changes are shown in FIG. **4**. No film growth is observed in Example 36. This is probably because both GOD and Mont were negatively charged and no adsorption due to the electrostatic interaction occurred. By contrast, in Example 35 the oppositely charged polymer ions and GOD molecules were premixed to form an admixed solution with a positive net charge, which enabled the alternate adsorptions with the negatively charged Mont.

This example also verifies that PEI, a flexible molecule present in the admixture, allowed the alternate layering of GOD with Mont (rigid or non-flexible molecules). Measurements were also conducted, for Example 37, of UV absorption at 665 nm on the film employed in Example 35. FIG. **5** shows that a regular increase in the UV absorption is observed with time, indicating a steady layering or self-assembly of GOD molecules. The subject examples thus demonstrate that the present invention of has enabled the alternate layer-by-layer assembling of likely charged materials as well as a hybrid-type alternate layering of an organic material and an inorganic material.

Examples 38–41: Alternate Layer-by-layer Assembly of Plural Non-flexible Materials

In Example 38 a GOD/PEI admixture (GOD:0.5 mg/ml, PEI:1 mg/ml) was prepared for alternate layer-by-layer assembly with Mont on the precoated quartz crystal microbalance. The resultant frequency changes are given in FIG. **6**, from which it is indicated that alternate GOD layers and Mont layers are successfully formed. Hitherto it has been impossible to perform an alternate layer-by-layer assembling with GOD and Mont as both substances are rigid or inflexible. According to the present invention the premixing of GOD with PEI allows the alternate layer-by-layer assembling of such two rigid substances in which PEI presumably serve as a glue.

In Example 39, GOD (0.5 mg/ml) and PEI (1 mg/ml) are premixed for an alternate layer-by-layer assembling with PSS on the quartz crystal microbatance. The resultant frequency changes are also given in FIG. **6**, from which it is indicated that alternate GOD layers and PSS layers are successfully formed. It has hitherto been impossible to conduct an alternate layer-by-layer assembling with GOD and PSS as these substances are likely charged. The premixing of GOD with PEI possibly result in the conversion of negative charge of GOD into a positive net charge, thus allowing the alternate layer-by-layer assembling with PSS, a polyanion.

In Example 40 and Example 41, enzymatic activity of GOD was determined by immersing the film obtained in Example 38 and Example 39 respectively in solutions containing glucose, POD and DA67 and measuring absorbance at 665 nm. The results are given in FIG. **7**, from which it is seen that the absorbance in creases as time lapses, demonstrating the enzymatic activity of GOD is effectively maintained within the film assemblies.

Example 42: Alternate Layer-by-layer Assembly Composed of Different Polymer Ions of Like Charges

In Example 42, an admixed GOD/PEI solution (GOD:0.5 mg/ml, PEI:0.01 mg/ml) was prepared for an alternate layer-by-layer assembling with PEI on the quartz crystal microbalance. The resultant frequency changes are given in FIG. **8**, from which it is seen that the alternate GOD layers and PEI layers were successfully formed. In this example, the electric charges of the admixed solution was dominated by the negatively charged GOD as the PEI concentration was adjusted to be relatively low, thereby enabling the alternate layering with the positively charged PEI. The premixing in accordance with the present invention thus makes it possible to obtain a solution of a functional molecule having any desired net electric charge, either positive or negative, by adjusting concentration of the functional molecule relative to that of an organic polymer ion in the solution. This leads to versatile selection of a substance or material with which the functional molecule is employed for an alternate layer-by-layer assembly.

As detailed in the above, according to the present invention functional molecules are premixed or admixed with polymer ions in a solution for an alternate layer-by-layer assembling process, thereby successfully constructing functional films composed of a variety of non-flexible functional molecules such as those which have been difficult to assemble by the conventional alternate layer-by-layer method. For example, a film composed of layers of dye molecules having a low molecular weight can be formed. It is also possible to construct, from an enzyme/polymer ion admixture, a layered-structure in which the association of the enzyme molecules are suppressed to exhibit an increased enzyme activity. Additionally, the premixing with polymer ions makes it possible to convert the net electric charge of functional molecules, thereby enabling an alternate layer-by-layer assembling with a substance having the same electrical charge as the functional molecules, such alternate layering being intrinsically impossible by the conventional method. Furthermore, according to the present invention there can be obtained an alternate layer-by-layer assembly made up of two or more different types of rigid molecules in a film, by the premixing with flexible polymer ions, such assembly having been impossible to obtain by the conventional method. The films of the present invention are composed of a layered-structure of a variety of functional molecules ranging from low molecular weight molecules to polymer molecules, providing good prospects of developing such devices as molecular devices and artificial reactors of the new generation.

What is claimed is:

1. A method for producing a multiple layered functional thin film which comprises:

immersing a solid support having an electric charge in a solution containing a mixture of functional molecules that provide a desired function in a physical or chemical process and charged polymer molecules, different from the functional molecules, that form a matrix to fix the functional molecules, which solution of functional molecules and charged polymer molecules having a net electric charge opposite to that of the solid support, to form a layer containing said functional molecules and said charged polymer molecules;

immersing the solid support and said layer containing said functional molecules and said charged polymer molecules in a solution containing charged polymer molecules having a net electric charge opposite to that of said solution containing the mixture of charged polymer molecules and functional molecules; and

repeating at least once said steps of immersing said solid support in a solution containing a mixture of charged polymer molecules and functional molecules and in a solution containing charged polymer molecules to form a desired multi-layered thin film.